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MICROPLASTIC-ASSOCIATED ORGANIC CONTAMINANTS IN THE BLACK SEA COASTAL ENVIRONMENT: OCCURRENCE OF OPFRS, PFAS AND BISPHENOLS

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Introduction

Microplastics (MPs) are persistent contaminants that are widely distributed in marine and coastal environments. In addition to their direct effects on aquatic organisms, MPs can interact with organic contaminants and contribute to their transport, persistence and bioavailability. Their large specific surface area, hydrophobicity and resistance to degradation enable the sorption of a broad range of chemical compounds from the surrounding environment. Consequently, MPs may act as vectors for contaminants such as organophosphate flame retardants (OPFRs), per- and polyfluoroalkyl substances (PFAS) and bisphenols. The Black Sea is particularly vulnerable to the accumulation of plastic debris and associated contaminants due to its semi-enclosed nature, intense coastal activity and significant anthropogenic pressure. However, information regarding the occurrence of organic contaminants associated with MPs along the Romanian Black Sea coast remains limited. This study aimed to investigate the presence of OPFRs, PFAS, and bisphenols associated with coastal MPs collected from several stations along the Romanian shoreline and to assess the potential role of MPs as carriers of these contaminants.

Materials and methods

Microplastic particles were collected from several coastal stations along the Romanian Black Sea shoreline, including Eforie Nord, Eforie Sud, and Tuzla. The collected material was characterized using Raman spectroscopy, and the resulting spectra were compared with reference spectra from an in-house spectral library generated from certified polymer standards. For the chemical analysis, MPs extracts were prepared using methanol, evaporated to dryness, and reconstituted in acetonitrile before analysis by liquid chromatography-tandem mass spectrometry (LC-MS/MS). The analytical workflow targeted three groups of organic contaminants: OPFRs, bisphenols and PFAS. A limit of quantification (LOQ) of 0.5 µg/kg was obtained for the method. Method recovery ranged from 83% to 106%, while precision, expressed as repeatability, ranged from 3.2% to 5.6%, and reproducibility ranged from 9.6% to 11.4%.

Results and conclusions

Raman spectroscopy showed that approximately 80% of the analyzed microplastics were polyethene (PE) fibres (Figure 1), while the remaining particles consisted mainly of polypropylene and polystyrene. Following extraction, the samples were analyzed by LC-MS/MS.

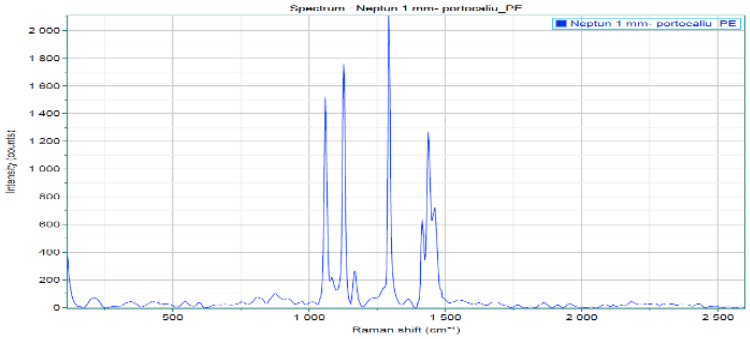


Figure 1 - Polyethene fibres from Neptun shoreline

The LC-MS/MS results confirmed the occurrence of compounds from all three investigated classes, with concentrations varying among the sampling stations (Figure 2). The highest concentrations were associated with long-chain PFAS, particularly PFTrDA at Eforie Sud. A comparatively high concentration of BPS was also identified at Mamaia suggesting localised anthropogenic influence and confirming the potential of microplastics as carriers of organic contaminants in the marine environment.

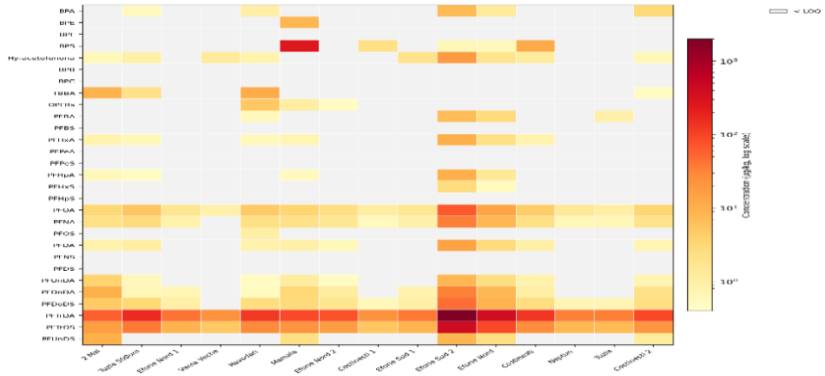


Figure 2 - Spatial distribution of OPFRs, PFAS and bisphenols in coastal microplastics (log-scale heatmap)